Second Virial Coefficients of Eight Compounds in the Range 40° to 200°C.

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The compressibility of *n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, benzene, acetone, carbon disulfide, and perfluoro-methyl-cyclohexane were determined in the range 40° to 200° C. and 200 to 800 mm. of Hg by a technique which is a combination of the constant volume and variable volume methods. The results agree with the virial equation of state $PV/RT = z = A + B/V + \dots$, from which the second virial coefficients were calculated.

AT SUFFICIENTLY low pressures, a gas may be represented by the relatively simple system of rigid bodies possessing potentials which interact with the potentials of neighboring bodies. The properties of real gases at low pressures may therefore be interpreted in terms of molecular dimensions and interaction potentials. Under these conditions, only the first two terms may be retained in the virial equation of state

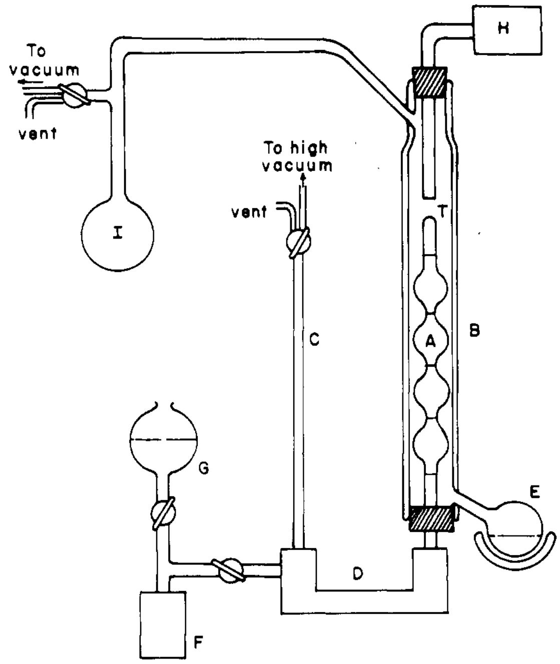

Figure 1. Experimental apparatus

- *A.* Calibrated sample tube
- *B.* Silvered vacuum jacket
- *C.* Manometer
- *D.* Block with pressure seals
- *E.* Boiling flask and heater
- *F.* Bellows for adjusting level of mercury
- *G.* Mercury reservoir
- *H.* Platinum resistance thermometer connected to a Mueller bridge
- *I.* Vacuum ballast
- *T.* Calibrated capillary tip in which the quantity of the sample was determined

$$\frac{PV}{RT} = z = A + \frac{B}{V} + \dots \qquad (1)$$

where V is the molecular volume, and A and B are the first and second virial coefficients. When Equation 1 applies, a plot of the compressibility z against $1/V$ at sufficiently low pressures should give a straight line whose intercept is A and whose slope is B. As the system pressure approaches zero, the gas approaches ideal behavior and, in the limit, the compressibility $z = A = 1$ at all temperatures.

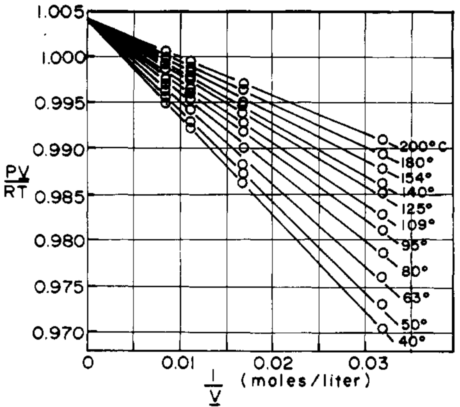

Figure 2. Isotherms for *n*-pentane

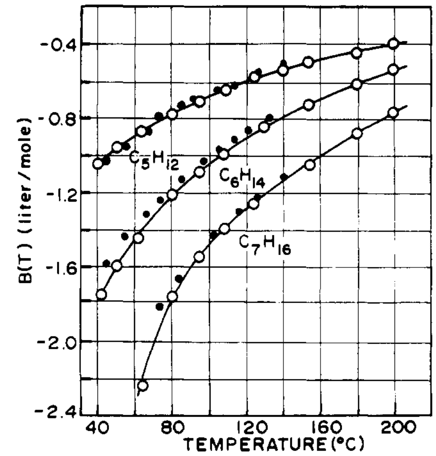

Figure 3. Second virial coefficients for *n*-pentane, *n*-hexane, and *n*-heptane

○ This study
● Reference (*8*)

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EXPERIMENTAL

Low-pressure compressibilities are usually determined by the constant volume (*9*) or the variable volume method (*6*). Various buoyancy methods have also been used (*1*, *3*). The technique developed for this study was a combination of the constant volume and the variable volume methods. This technique afforded precise determination of volume, while eliminating the need for frequent changes in the quantity of the sample.

The determination of the sample volume was carried out in tube A (Figure 1). This consisted of four glass bulbs, 25-mm. I.D., interconnected by smaller tubes, 10-mm. I.D. Each of these tubes was etched with a line approximately 0.001 mm. wide. The volume of each bulb and that of the capillary tip, T, 1-mm. I.D., were previously calibrated with respect to these etched lines. Sample tube A was maintained at a constant temperature by boiling a pure liquid in a side-arm flask attached to the silvered vacuum-jacketed tube, B. The pressure of the boiling liquid could be varied between 250 and 760 mm. of Hg, thus covering a temperature range of about 30° C. The temperature was measured to within ±0.005° C. with a platinum resistance thermometer. Pressures were computed from the difference in the mercury levels in sample tube A and manometer C. A precision cathetometer reading to 0.01 mm. was used. All pressures were corrected for the vapor pressure of mercury.

A sample of the pure liquid was confined over mercury in the calibrated tip, T, and its quantity determined by measuring its length at a known temperature. The volume determinations were done by vaporizing the liquid sample, and the pressure was adjusted until the vapor was precisely confined within the limits of a calibrated segment of tube A. The precision of the volumetric measurements was established as being better than one part in ten thousand.

Table I. Properties of Compounds Studied

Compound	Purity, Mole %	Refractive Index, 20° C.		Vapor Pressure, Mm. Hg		Source
		Exptl.	Lit.	Exptl.	Lit.	
n-Pentane	99.84 ± 0.16	...	...	...	...	[a]
n-Hexane	99.85 ± 0.15	...	...	...	...	[a]
n-Heptane	99.93 ± 0.07	...	...	...	...	[a]
Cyclohexane	99.94 ± 0.06	...	...	...	...	[a]
Benzene	99.93 ± 0.07	...	...	...	...	[a]
Acetone	99.90 ± 0.05[d]	1.3591	1.3591 (*5*)	612.6, 50° C.	612.6, 50° C. (*5*)	[b]
Carbon disulfide	99.90 ± 0.05[d]	1.6276	1.6276 (*5*)	760.10, 46.25° C.	760.0, 46.25° C. (*5*)	[b]
Perfluoro-methyl-cyclohexane[e]	99.90 ± 0.08[d]	1.2815	1.2816 (*2*)	760.0, 76.38° C.	760.0, 76.33° C.	[c]

[a] Phillips Petroleum Co., used as received. [b] Reagent grade chemicals, purified by fractional distillation. [c] E. I. DuPont de Nemours Co., purified by fractional distillation. [d] Estimated from refractive index and vapor pressure measurements. [e] Density, 20° C., 1.8045 gram/cc. exptl. Lit. (*2*) 1.7996.

Table II. Second Virial Coefficients of Eight Compounds Investigated in the Temperature Range 40° to 200° C.

n-Pentane		*n*-Hexane		Benzene		Acetone	
Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole
40.00	1.050			40.00	1.565	40.00	1.575
50.00	0.960	42.00	1.750	50.00	1.350	50.00	1.375
63.00	0.875	50.00	1.590	58.00	1.215	64.00	1.200
80.00	0.785	62.00	1.450	62.00	1.150	80.00	1.065
95.00	0.715	80.00	1.205	80.00	0.945	95.00	0.920
109.00	0.655	95.00	1.090	95.00	0.840	109.00	0.800
125.00	0.575	109.00	0.995	109.00	0.765	125.00	0.700
140.00	0.535	130.00	0.850	125.00	0.720	140.00	0.630
154.00	0.500	154.00	0.730	140.00	0.645	155.00	0.555
180.00	0.445	179.97	0.615	154.00	0.610	180.00	0.455
200.00	0.400	200.00	0.530	180.00	0.550	200.00	0.400
				200.00	0.510		

n-Heptane		Cyclohexane		Carbon Disulfide		Perfluoro Methyl Cyclohexane	
Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole	Temp., ° C.	–B liters/ mole
40.00	3.735	43.43	1.625	40.00	0.810	40.00	2.610
50.00	2.765	52.92	1.365	50.00	0.700	50.00	2.140
63.00	2.240	63.25	1.225	64.00	0.605	64.00	1.595
80.00	1.760	80.00	1.045	80.00	0.480	80.00	1.370
95.00	1.555	95.00	0.940	95.00	0.430	95.00	1.145
109.00	1.385	108.85	0.885	109.00	0.380	109.00	1.065
125.00	1.265	123.48	0.795	125.00	0.335	125.00	0.905
154.00	1.045	137.90	0.690	140.00	0.310	140.00	0.815
180.00	0.880	155.00	0.625	154.00	0.270	154.00	0.730
200.00	0.775	180.00	0.540	180.00	0.230	180.00	0.600
		200.00	0.490	200.00	0.195	200.00	0.505

The over-all precision in the compressibility was better than six parts in ten thousand.

Liquid samples were transferred to the capillary tip by sealing the calibrated sample tube, A, to a high-vacuum line. The sample tube was then heated to ensure that its inside surface was free from adsorbed gases. A small quantity of the deaerated sample was distilled into the capillary tip for rinsing purposes, then distilled out and discarded. The tip was rinsed twice before a final sample was retained. Mercury was then distilled over the sample, the sample tube disconnected from the vacuum line, and mounted in the apparatus, as shown in Figure 1. The sources and purities of the compounds used in this investigation are given in Table I.

RESULTS AND DISCUSSION

P-V-T measurements on the vapor of eight compounds were made covering the temperature range 40° to 200° C. and the pressure range 160 to 1000 mm. of Hg. When the compressibility, *z*, was calculated and plotted against $1/V$, it was evident that the plots were linear; hence, the third virial coefficient and all higher coefficients were small enough to be neglected. The isotherms did not converge to unity, but to a slightly higher value ranging between 1.001 and 1.004. This was the case with all eight compounds investigated. Figure 2 shows a typical plot. This consistent error of about 0.2% in the value of the mean intercept showed no temperature or pressure correlation. Further investigation showed that this could not be due to the solubility of the sample in mercury, leading to the conclusion that the determination of the mass of all the samples was in error by about 0.2%, probably due to an erroneous meniscus correction. The authors had assumed that the meniscus formed a segment of a sphere. This error was insignificant in relation to the volume of the vapor in the bulbs of tube A, but was appreciable in relation to the volume of the liquid sample in tip T.

This error was corrected for by subtracting from the computed value of the compressibility the difference between the mean value of the intercept and unity. This procedure essentially amounted to adjusting the ordinate, or the compressibility value, downward so that the mean intercept was equal to unity. The *B* values were then determined by a least squares method, taking the intercept as unity as an experimental point. The corrected results are given in Table II and plotted in Figures 3 to 8.

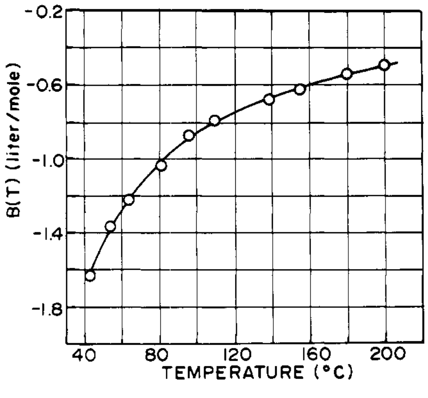

Figure 4. Second virial coefficient for cyclohexane, C_6H_{12}

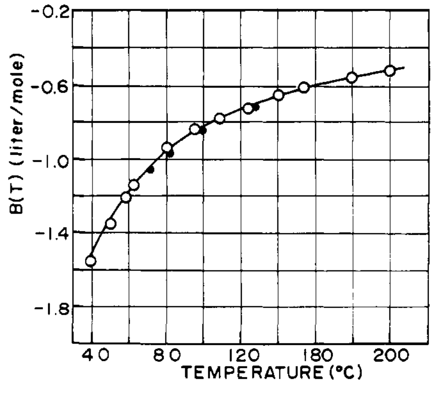

Figure 5. Second virial coefficient for benzene, C_6H_6

○ This study

● Reference (4)

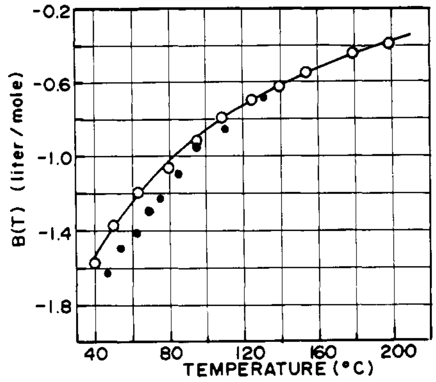

Figure 6. Second virial coefficient for acetone, C_3H_6O

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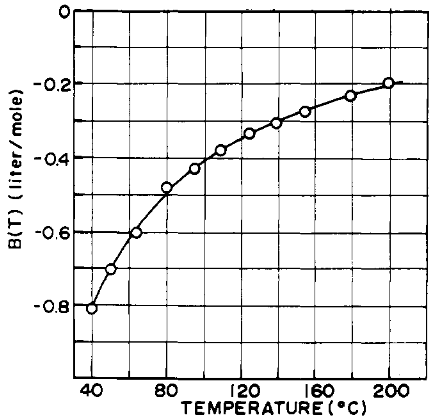

Figure 7. Second virial coefficient for carbon disulfide, CS_2

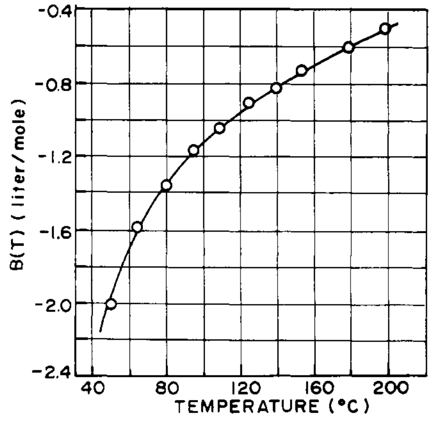

Figure 8. Second virial coefficient for perfluoro-methyl-cyclohexane, C_7F_{14}

Table III. Literature Values of the Second Virial Coefficients

Temp., ° C.	−B Liters/ Mole
n-Pentane (*8*)	
25.0	1.194
32.9	1.117
44.9	1.011
55.8	0.923
65.8	0.863
75.8	0.800
84.8	0.758
95.4	0.701
105.7	0.652
115.2	0.612
127.8	0.578
140.4	0.517
n-Hexane (*8*)	
44.8	1.598
55.8	1.419
64.5	1.338
74.8	1.235
85.3	1.144
97.4	1.050
104.5	0.992
113.5	0.928
122.7	0.880
136.9	0.800

Temp., ° C.	−B Liters/ Mole
n-Heptane (*8*)	
76.2	1.819
85.1	1.691
95.3	1.560
104.9	1.446
115.9	1.325
127.6	1.212
140.5	1.108
Benzene (*4*)	
70.0	1.035
80.0	0.971
100.0	0.852
100.0	0.839
125.0	0.733
Acetone (*7*)	
46.2	1.644
56.3	1.527
61.8	1.406
67.8	1.362
68.2	1.342
78.0	1.257
88.0	1.134
95.2	0.965
111.8	0.854
132.4	0.651

A few checks on the calculated values of B were made by using

$$\lim_{V\to\infty} (z-A)V$$

The quantity $(z - A)V$ was plotted against $1/V$. The values of B, as given by the intercepts, were in agreement with the values obtained as explained above. The horizontal slope indicated that the third virial coefficient was, within the experimental error, equal to zero.

The values of the second virial coefficient, B, reported in the literature in the temperature range covered in this study are given in Table III and are plotted in Figures 3, 5, and 6. There seems to be close agreement with the authors' results, except for acetone at low temperatures.

The calculation of the intermolecular potential parameters will be discussed in a forthcoming paper.

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Density, Electrical Conductivity, and Vapor Pressure of Concentrated Phosphoric Acid

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Density and specific conductivity for H_3PO_4 in the concentration range 86 to 102 wt. % from room temperature to 170° C. are presented. The vapor pressure portion gives data for 77 to 102 wt. % H_3PO_4 for temperatures between 130° and 170° C. In each case, equations are given which provide a good least squares fit to the experimental data.

THE DENSITIES of phosphoric acid solutions have been determined by others (*2, 3*) at concentrations up to 92% and at temperatures up to 80° C. This work concerns the experimental determination of densities at higher concentrations and higher temperatures.

EXPERIMENTAL

Pycnometers of 25-ml. capacity were calibrated against water at 25.00° C. The cubical coefficient of expansion of borosilicate glass was used to calculate the volumes at higher temperatures. All weights were corrected to vacuum. Temperature was controlled to 0.01° C. and measured to 0.1° C. in oil thermostats. Solutions of phosphoric acid were prepared by dehydration of the C.P. grade at 150° to 175° C. in ovens. To avoid contamination, preparations were made in FEP bottles (fully fluorinated ethylene-propylene copolymer). The bottles were preconditioned at 150° to 175° C. Then, acid of known composition (usually 85.1%, determined by repeated pH titration) was weighed into them. The acid composition was calculated from the weight loss of water after heating. The concentrated phosphoric acid solutions were stored in FEP bottles at room temperature before use. The experimental data is given in Table I.

CORRELATION OF DENSITY DATA

Plots of the data in Table I reveal the density to be a linear function of the temperature, including the points at 25° C. Furthermore, the density is also linear in the concentration over the limited range studied here.

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